



A kinetic study on the effects of alkaline earth and alkali metal compounds for catalytic pyrolysis of microalgae using thermogravimetry



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HIGHLIGHTS

- Alkali and alkaline earth metals compounds can promote the degradation of microalgae organic matters.
- Alkali and alkaline earth metals compounds can increase the initial decomposition temperatures of microalgae pyrolysis.
- Alkali and alkaline earth metals compounds can affect the microalgae pyrolysis overall activation energy.

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ABSTRACT

In this paper, thermogravimetric (TG) analysis and kinetic modeling are applied to study the effects of alkaline earth and alkali metal compounds on catalytic thermal decomposition of microalgae. When alkaline earth and alkali metal compounds are added, the initial thermal degradation temperatures increased by about 3.2–10.2 K, and the final temperatures reduced by about 3.5–9.4 K. The results show that CaO, MgO, K₂CO₃, BaCO₃ and Na₂CO₃ may shorten the time of pyrolysis, implying that alkaline earth and alkali metal compounds may promote the process of thermal degradation of organic matters. The first maximum weight loss rate is in the order of Na₂CO₃ > CaO > K₂CO₃ > BaCO₃ > MgO > no additive. E_m (weight means activation energy) varies from 99.60 to 134.05 kJ mol⁻¹, which implies ignorable overall activation energies (E_m) after alkaline earth and alkali metal compounds are added.

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1. Introduction

Biofuel receives increasingly concerns from governments and scientists all over the world, due to its ease of treatment, storage and transportation [1]. At present, grain, a common raw material for biofuel production, becomes a threat to food supply, which further, affects the social and economic stability. It is clearly stated in the “Corn processing project on strengthening the management of emergency notice” that China will insist on promoting non-grain-based biofuel industry [2]. Microalgae are single-cell algae and rich in fat, protein and carbohydrates, besides it can effectively convert CO₂, H₂O, and inorganic salts into organic substances through solar energy. Compared with other biomass resources, microalgae has the following distinctive characteristics [3–6]: high photosynthetic efficiency and environmental adaptability, short

growth cycle, independence from soil, automatic breeding process, capability to produce high-molecular-weight hydrocarbons with high calorific value and very little sulfur and nitrogen.

To make the best use of all algae cells, several researchers began to convert algae into high-energy-density liquid biofuel through thermal degradation technology. In 1993, Ginzburg [7] successfully applied thermal decomposition of microalgae for low-nitrogen liquid substance, which produced a high-quality low-sulfur bio-oil. Other researchers have made further studies and progresses in the microalgae pyrolysis of biofuel [8–11]. According to previous research results, in order to produce liquid biofuel from microalgae, the maximum liquid biofuel production portion of heterotrophic microalgae is 57.9% and autotrophic microalgae is 35.83%, with others as gas or solid. Therefore, further exploration is necessary to improve the overall bio-oil yield (conversion level).

The application of alkali and alkali-earth salts in coal and other biomass catalytic pyrolysis has been extensively studied [12–15]. The results show that the oil production rate is higher, with the addition of catalyst in the process of biomass pyrolysis. With

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intermediate temperatures, K^+ and Ca^{2+} catalytic pyrolysis mainly occurs in the solid phase, and only a very small amount of liquid or gas is generated. Different categories of ion selective catalytic reaction are formed and the process of molecular bond breaking in fission and disproportionation reaction is accelerated. This feature provides a guarantee for the preparation of bio-oil conditions. Therefore, catalyst can improve the conversion rate of biomass pyrolysis process. However, the catalysis of alkaline earth and alkali metal compounds for microalgae thermal decomposition has not been addressed and is worth for further studies.

This paper will discuss the microalgae catalytic pyrolysis with alkaline earth and alkali metal compounds. The powdery microalgae was mixed with alkaline earth and alkali metal compounds (including $BaCO_3$, K_2CO_3 , Na_2CO_3 , MgO , and CaO), respectively. The catalytic thermal degradation was conducted by a TG analyzer. The heating rate of TG analyzer is $10\text{--}30\text{ K min}^{-1}$, the reaction atmosphere is nitrogen (N_2), and the temperature range is from ambient temperature to $1000\text{ }^\circ\text{C}$. The kinetic parameters are decided by Flynn Wall Ozawa (FWO) and Kissinger Akahira Sunose (KAS) methods, to evaluate the effects of catalytic pyrolysis.

2. Materials and methods

2.1. Materials

The microalgae used in this study were *Chlorella vulgaris* produced by Jiangmen City Yue Jian Biotechnologies Company Limited in China. Barium Carbonate ($BaCO_3$), potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), Magnesia (MgO) and calcium oxide (CaO) were used as catalyst in the experiments.

Samples of *Chlorella vulgaris*, alkaline earth and alkali metal compounds were kept in a $105\text{ }^\circ\text{C}$ drier for about 24 h, were then grinded into particles with no more than 200 microns. After the above pretreatment, the samples were laid in a container with desiccant.

Additives were mixed on microalgae through mechanical mixing method, the specific processes are as follows: take samples that weigh 200 g, and additive that weighs 2 g, then they were poured into a mortar in order to mix them thoroughly, and were then grinded; finally, the mixed microalgae sample was placed in a vacuum oven for 14 h, and dried at $80\text{ }^\circ\text{C}$.

The ultimate analysis and proximate analysis were tested according to GB/T212-2008, GB211-84 and ASTM D5373-08, respectively. Heat figures were valued based on ASTM D5468-02 and ASTM E870-82. The proximate analysis, ultimate analysis and low calorific value were listed in Table 1.

2.2. Equipment and experimental procedures

A thermogravimetric Analyzer (model: NETZSCH STA 409 PC Luxx) was used for TG analysis. A crucible, placed on sample carrier, was made of Al_2O_3 . The thermocouple of type S was welded on heating metal coil in a furnace, with the temperature reproducibility $\pm 3\text{ }^\circ\text{C}$, and the temperature precision was $\pm 0.1\text{ }^\circ\text{C}$. The

balance mass precision was 0.001 mg. In the crucible, about 3.5 mg samples were placed uniformly, and the temperature was linearly raised from ambient temperature (about $35\text{ }^\circ\text{C}$) to $1000\text{ }^\circ\text{C}$ with a heating rate of $30\text{ }^\circ\text{C min}^{-1}$. There was no additional hold at a temperature. The pyrolysis atmosphere of desired gas flow rate was a constant of 100 mL min^{-1} . Transmission error of the experimental system was 0.01%.

2.3. Characteristic parameters of temperatures and increment of weight loss

The onset and end thermal degradation temperatures represent how severe the reaction was. The peak temperature (T_p), corresponding to the maximum weight loss rate ($d\alpha/dt$), was related to the fuel property. The onset temperature (T_0) of microalgae thermal decomposition was defined as the temperature at a weight loss rate of 5%. The end decomposition temperature (T_f) was defined as the temperature at a weight loss rate of 95%. DTG_p was the differential thermalgravity value at a peak temperature.

Δm [16] was obtained to further explain the effectiveness of these five additives on the conversion of microalgae samples as.

$$\Delta m = m_c - m_w \quad (1)$$

where Δm as the increment of weight loss after mixing alkali and alkaline earth with microalgae samples, m_c as the weight loss of microalgae samples with the addition of additives, and m_w as the weight loss of the microalgae samples under a uniform temperature. Δm represented the 'level' of catalytic impact of additive, such as alkali and alkaline earth. TG weightlessness unit was wt.%.

2.4. Kinetic analysis of the microalgae pyrolysis

The conversion rate of single reaction model [17] can be described as follows:

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n \exp\left(-\frac{E}{RT}\right) \quad (2)$$

α is the fractional conversion of combustible in microalgae at the time t , and is given as $\alpha = (m_0 - m)/(m_0 - m_\infty)$; m_0 , m_∞ , m refer to the onset, end residual amount, and present of microalgae specimen, respectively; R , which equals to $8.314\text{ J mol}^{-1}\text{ }^\circ\text{C}^{-1}$, is a universal gas constant, and n is reaction order and T is Kelvin temperature.

In this paper, an isoconversional model was used to carry out all experimental data with different heating rates. The activation energy was figured out from a series of dynamic data according to the isoconversional model by Flynn Wall Ozawa (FWO) and Kissinger Akahira Sunose (KAS).

The following formula is based on FWO:

$$\ln \beta = \ln \left[\frac{0.0048AE_\alpha}{g(\alpha)R} \right] - 1.0516 \frac{E_\alpha}{RT} \quad (3)$$

where, α is a constant, $\ln \beta$ vs. $1/T$ obtained at three heating rates obtain a straight line, and the slope evaluates apparent activation energy.

The following formula is based on KAS:

$$\ln \left(\frac{\beta}{T^2} \right) = \ln \left[\frac{AR}{g(\alpha)E_\alpha} \right] - \frac{E_\alpha}{RT} \quad (4)$$

E_α for different fractional conversion can be figured out from a plotting $\ln(\beta/T^2)$ vs. T^{-1} .

Table 1

Ultimate, proximate analyses and calorific value of *Chlorella vulgaris* (wt.% on dry basis).

Ultimate analysis (wt.%)					Proximate analysis (wt.%)			LCV (MJ kg ⁻¹)
C	H	O	N	S	Volatile	Ash	Fixed carbon	
47.84	6.41	25	9.01	1.46	55.37	10.28	34.35	21.88

Note: LCV, low calorific value.

3. Results of the experiment

3.1. Effects of additives on the amount of solid residues in microalgae catalytic pyrolysis

After analyzing the TGA results, the effects of K_2CO_3 , Na_2CO_3 , CaO , $BaCO_3$ and MgO on the amount of solid residues can be observed from the process of microalgae pyrolysis. Fig. 1 shows the residual mass percents of microalgae samples with and without the additional alkaline earth and alkali metal compounds, under the end temperature (1000 °C) of thermal degradation. The amount of solid residues is 1.35 mg (with no additive), 1.05 mg (K_2CO_3), 0.82 mg (Na_2CO_3), 1.11 mg ($BaCO_3$), 1.15 mg (CaO) and 1.35 mg (MgO) respectively. Under the end thermal decomposition temperature, the main component of solid residue is ash and char, the solid residue rate follows the order of no additive > MgO > CaO > $BaCO_3$ > K_2CO_3 > Na_2CO_3 .

3.2. Effects of additives on characteristic parameters of temperatures for microalgae catalytic pyrolysis

Characteristic temperatures include initial temperature (T_0), end temperature (T_f) and peak temperature (T_p) of thermal decomposition. In Table 2, it can be seen that alkaline earth and alkali metal compounds can increase the T_0 by approximately 3.2–10.2 K, which means that the addition of alkaline earth and alkali metal compounds may restrain the initial thermal degradation of microalgae. T_f reduced by about 3.5–9.4 K with the addition of alkaline earth and alkali metal compounds. The results revealed that MgO , K_2CO_3 , $BaCO_3$, Na_2CO_3 and CaO may shorten the pyrolysis time.

MgO had weak effects on microalgae pyrolysis, as analogous T_p of samples was discovered. However, T_p decreased by approximately 2.5 K due to the addition of CaO , indicating that the addition of CaO may promote the degradation of protein and polysaccharides. T_p increased by approximately 0.3 K due to the addition of Na_2CO_3 , which indicated that Na_2CO_3 may not affect the degradation of protein and polysaccharides. T_p decreased by approximately 0.6–0.7 K due to the addition of K_2CO_3 and $BaCO_3$, which illustrated the active effects of K_2CO_3 and $BaCO_3$ on the pyrolysis of microalgae. Therefore, the properties of microalgae samples might be transformed because of the addition of CaO , K_2CO_3 and $BaCO_3$.

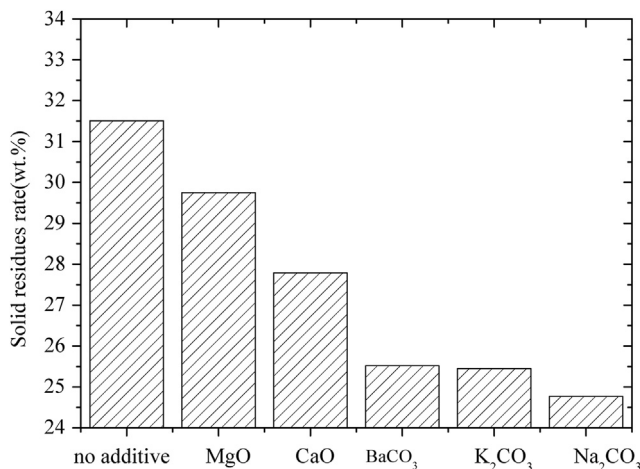


Fig. 1. The rate of solid residue productions from microalgae pyrolysis (1% catalyst; atmosphere: nitrogen; heating rate of 30 K/min).

Table 2

Typical characteristic temperature parameters of microalgae pyrolysis with/without alkali and alkaline earth metals compounds (1% catalyst; atmosphere: nitrogen; heating rate of 30 K/min).

Catalyst	T_0 (°C)	T_f (°C)	T_p (°C)	DTC _p (% min ⁻¹)
No catalyst	268.7	432.2	341.8	11.57
K ₂ CO ₃	271.9	428.7	341.2	12.43
Na ₂ CO ₃	275.1	422.8	342.1	13.04
BaCO ₃	274.3	428.7	341.1	11.95
CaO	278.9	427.4	339.3	12.84
MgO	272.9	431.7	341.7	11.90

Note: T_0 , pyrolysis initial temperature; T_f , pyrolysis end temperature, T_p , pyrolysis peak temperature; DTC_p, differential thermalgravity value at a peak temperature.

3.3. Effects of alkaline earth and alkali metal compounds on fractional conversion of microalgae catalytic pyrolysis

Fig. 2 shows the effects of alkaline earth and alkali metal compounds have on the weight loss (or fractional conversion) during microalgae catalytic pyrolysis as a function of temperature. It indicated that the weight loss mainly occurred in the range of temperature from 127 to 527 °C for microalgae samples without and with additive. When K_2CO_3 , Na_2CO_3 , $BaCO_3$, CaO or MgO were mixed with microalgae samples separately, the weight loss curves were transformed at various levels, suggesting that the effects of these cheap alkali and alkaline earth on microalgae thermal catalytic decomposition were different.

The calculated results were shown in Fig. 2. It indicated that Δm of MgO added in sample was close to 0 when the temperature was between 285 °C and 340 °C, and then decreases slightly as the temperature increases. CaO improves the fractional conversion of microalgae in the temperature range of below 177 °C and above 487 °C. The addition of Na_2CO_3 , K_2CO_3 and $BaCO_3$ into microalgae samples significantly strengthens the transformation of microalgae samples under a lower temperature (about 237 °C).

3.4. Effects of additives on weight loss rates of microalgae catalytic pyrolysis

Fig. 3 shows the variation of weight loss rates (da/dt) with the existence and absence of alkaline earth and alkali metal compounds in the pyrolysis of microalgae. Table 2 shows the maximum weight loss rate at the stage of decomposition.

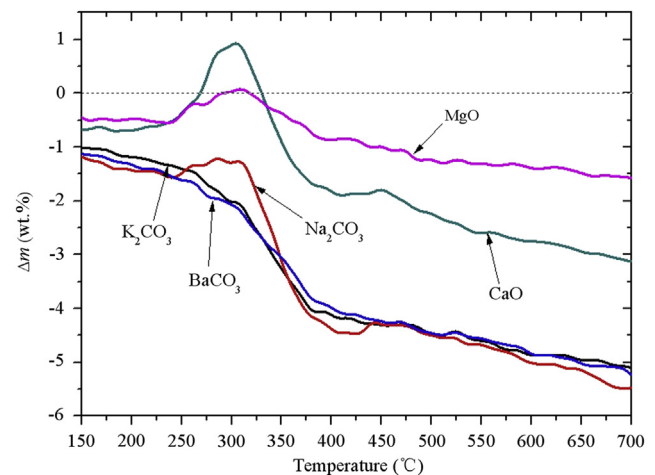


Fig. 2. Variation of Δm (weight loss with additives minus weight loss of sample) of microalgae pyrolysis (1% catalyst; atmosphere: nitrogen; heating rate of 30 K/min).

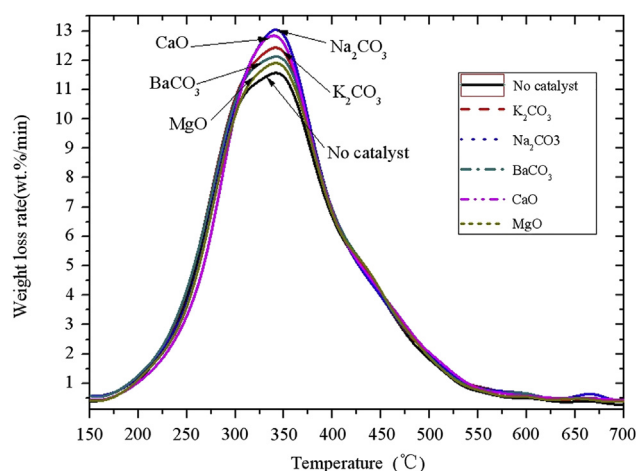


Fig. 3. Weight loss rates of microalgae pyrolysis with/without addition of alkaline earth and alkali metal (1% catalyst; atmosphere: nitrogen; heating rate of 30 K/min).

It can be seen from Fig. 3 that Na_2CO_3 , CaO , BaCO_3 , K_2CO_3 and MgO affect the weight loss rates of microalgae catalytic decomposition. The addition of Na_2CO_3 and CaO promotes the reaction rates extensively when the temperature is between 300 and 375 °C. In Table 2, the first maximum weight loss rate increases with the addition of alkaline earth and alkali metal compounds, following the order of $\text{Na}_2\text{CO}_3 > \text{CaO} > \text{K}_2\text{CO}_3 > \text{BaCO}_3 > \text{MgO} > \text{no additive}$.

3.5. Effects of additives on kinetic parameters of microalgae catalytic pyrolysis

Kinetic parameters were figured out by Eq. (5), on account of the first order reaction supposition in the microalgae pyrolysis process. To study the impacts of alkaline earth and alkali metal compounds have on the kinetic parameters of microalgae thermal degradation, the weighted average activation energy (E_m) was figured out and applied to analyze the microalgae entire reactivity [18],

$$E_m = F_1 \times E_1 + F_2 \times E_2 + \dots + F_n \times E_n \quad (5)$$

where E_1 to E_n are the activation energy at each stage, and F_1 to F_n are accordingly weight loss quantities. The results are listed in Table 3.

As indicated in Table 3, the pyrolysis of microalgae samples, with/without the addition of alkaline earth and alkali metal compounds, occurs in two sections with various relative weight loss

quantities. In the low-temperature region (primary decomposition section), the relative weight loss quantity content of microalgae varies from 51.30% to 59.50% with the addition of alkaline earth and alkali metal compounds. In the high-temperature region (secondary decomposition section), the relative weight loss content of microalgae varies from 30.22% to 35.22%. It suggests that a higher temperature and a longer time of reaction were necessary for larger activation energy. For microalgae samples, the activation energies (E) were $66.61 \text{ kJ mol}^{-1}$ and $208.41 \text{ kJ mol}^{-1}$ in primary and secondary pyrolysis section, respectively. Activation energies changed by $1\text{--}3.57 \text{ kJ mol}^{-1}$ (from 65.75 to $69.32 \text{ kJ mol}^{-1}$), and $46.65\text{--}63.19 \text{ kJ mol}^{-1}$ (from $197.17 \text{ kJ mol}^{-1}$ to $260.36 \text{ kJ mol}^{-1}$) in primary and secondary degradation sections, respectively, and increased by up to $51.95 \text{ kJ mol}^{-1}$ in secondary decomposition section with the addition of alkaline earth and alkali metal compounds. The results show that the addition of alkaline earth and alkali metal compounds may reduce the time of protein and polysaccharides pyrolysis, while increase the entire reaction time of microalgae pyrolysis. However, an increased overall activation energy (E_m) was discovered (from $99.60 \text{ kJ mol}^{-1}$ to $134.05 \text{ kJ mol}^{-1}$), meaning that the effects of alkaline earth and alkali metal compounds on the E_m could be ignored. In the range of homologous temperature, compared with the condition without additive, the addition of Na_2CO_3 , CaO , BaCO_3 , K_2CO_3 or MgO also brought about a decrease of pre-exponential factor (A). The variation of E and A indicated that the chemical structure of microalgae might change due to the addition of alkaline earth and alkali metal compounds, and different alkaline earth and alkali metal compounds had different catalytic characteristics in different temperature ranges. The correlation coefficient (R) was about 0.9918–0.9919, which illustrated that the experimental data was in accordance with the theoretical results.

4. Discussion

Pyrolysis is thermal decomposition occurring in the absence of oxygen. Three products always go with this process: gas, liquid and solid. Usually, solid residues contain two kind of matters: char and ash. Metal oxides, such as MgO , which can prevent the formation of hydrocarbon stable chemical structures and speed up degradation of hydrocarbon [19]. Therefore, as shown in Fig. 1, the formation temperature of solid residue was lowered by alkaline earth and alkali metal compounds, indicating that alkaline earth and alkali metal compounds may accelerate the degradation rate of organic matters. Even 1 wt.% K_2CO_3 begin to decompose at the temperature of 900 °C, but its solid residues productions are 6.74 wt.% less than that of without catalyst. As a result, less solid residue was gained.

Table 3

The kinetics parameters of microalgae pyrolysis with/without addition of alkali and alkaline earth metals compounds (1% catalyst; atmosphere: nitrogen; heating rate of 30 K/min).

Catalyst	Temperature range (K)	F (wt.%, daf)	A (s^{-1})	E (kJ mol^{-1})	RO	R	E_m (kJ/mol)
No catalyst	150.0–432.2	54.50	$4.25\text{E}+01$	66.61	2.4	0.9998	109.70
	432.2–700.0	35.22	$7.53\text{E}+08$	208.41	1.0	0.9978	
K_2CO_3	150.0–428.7	51.30	$4.16\text{E}+01$	66.31	2.4	0.9989	134.05
	428.7–700.0	38.42	$1.41\text{E}+11$	260.36	1.0	0.9978	
Na_2CO_3	150.0–422.8	55.60	$4.91\text{E}+01$	68.32	2.4	0.9999	105.26
	422.8–700.0	34.12	$1.92\text{E}+08$	197.17	1.0	0.9976	
BaCO_3	150.0–428.7	59.30	$3.93\text{E}+01$	65.75	2.4	0.9978	99.60
	428.7–700.0	30.42	$2.34\text{E}+08$	199.26	1.0	0.9945	
CaO	150.0–427.4	59.50	$5.19\text{E}+01$	69.32	2.4	0.9918	105.45
	427.4–700.0	30.22	$1.04\text{E}+09$	212.45	1.0	0.9994	
MgO	150.0–431.7	59.40	$4.42\text{E}+01$	67.29	2.4	0.9978	104.76
	431.7–700.0	30.32	$1.08\text{E}+09$	213.71	1.0	0.9959	

Note: F , relative weight loss; E , activation energy in each stage; A , pre-exponential factor; RO, reaction order; R , correlation coefficient; E_m , weight mean activation energy.

The thermogravimetric (TGA) and differential thermogravimetric (DTG) curves revealed two decomposition steps that are common to all studied work conditions. The first stage represented the main devolatilization reactions, where most of the sample weight was lost as volatile matter (160–450 °C). Three processes can be distinguished in this stage: at the first process, being the low-temperature peak (180 °C) mainly associated to the decomposition of protein and soluble polysaccharide whereas secondary the higher temperature peaks (271 °C and 411 °C) would corresponded to the degradation of crude cellulose in the cell wall, thirdly are other insoluble polysaccharides and crude lipid [20]. Finally, the second stage took place at the temperatures above 450 °C leading to char formation [21]. Therefore, Table 2 shows that the first maximum weight loss rate (temperature range is 341.1–342.1 °C) is caused by crude cellulose degradation.

Due to the same reasons, as shown in Fig. 2, MgO has little positive effects on the microalgae catalytic thermal decomposition under a higher temperature. This result is well consistent with literature that MgO catalysis of coal pyrolysis is basically effective in higher-temperature regions [19]. CaO may facilitate the onset degradation of protein, soluble polysaccharide and further decomposition of insoluble polysaccharides and crude lipid. The addition of Na₂CO₃, K₂CO₃ and BaCO₃ into microalgae samples strengthens the transformation of microalgae samples under a lower temperature (about 237 °C); whereas it restrains crude cellulose degradation under a higher temperature (about 350 °C). The competing reactions lead to the constraint of MgO to the microalgae degradation. In the entire range of temperature, the active effects of CaO on the transformation of organic matters were discovered, and maintained steadily above 277 °C.

Concerning the pyrolysis mechanism at the surface of supported catalysts, it can be assumed that the catalyst causes the weakening of the intermolecular interaction of the polymeric chains. Catalyst, e.g. BaCO₃, can prevent the formation of hydrocarbon stable chemical structures, enable the tar easy to decompose, and can also speed up the degradation of hydrocarbon; Catalyst can weak the C–C bond and decrease the activation energy for pyrolysis reactions [22]. With the existence of catalysts in the microalgae samples, the volatile gases concentrations around the microalgae particle are higher, resulting in activation energy that can be lower than the sample without catalyst.

This study summarizes that the sequence of catalytic importance of alkaline earth and alkali metal compounds is not the same for onset, end, and the first maximum weight loss rate under nitrogen atmospheres. Therefore, the catalysis of alkaline earth and alkali metal compounds can enhance the conversion rate of microalgae pyrolysis process in terms of gaining more gas and liquid which are the raw materials of bio-oil.

5. Conclusions

According to TGA and kinetic studies, the following conclusions can be reached:

- (1) Under the end pyrolysis temperature (1000 °C), the rate of solid residue follows the order of no additive > MgO > CaO > BaCO₃ > K₂CO₃ > Na₂CO₃, indicating that alkaline earth and alkali metal compounds may accelerate the degradation rate of organic matters.
- (2) With the addition of alkaline earth and alkali metal compounds, initial decomposition temperatures increased by about 3.2–10.2 K, and the final temperatures reduced by about 3.5–9.4 K with the addition of alkaline earth and alkali metal compounds, revealing that CaO, MgO, K₂CO₃, BaCO₃ and Na₂CO₃ may shorten the pyrolysis time.

- (3) The first maximum weight loss rate follows the order of Na₂CO₃ > CaO > K₂CO₃ > BaCO₃ > MgO > No catalyst.
- (4) The overall activation energies (E_m) vary from 99.60 to 134.05 kJ mol⁻¹, which suggests that the effects of alkaline earth and alkali metal compounds on the overall activation energies (E_m) cannot be ignored.

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